

Influence of layer charge on swelling of smectites[☆]

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Abstract

Six separate processes control the swelling of smectites saturated with alkali and alkaline earth cations in aqueous systems. The basic mechanism and forces controlling each of the processes are different. Crystalline swelling occurs between smectite layers within quasicrystals and involves the intercalation of zero to four discrete layers of water molecules. A balance between strong electrostatic-attraction and hydration-repulsion forces controls crystalline swelling. The extent of crystalline swelling decreases with increasing layer charge. Double-layer swelling occurs between quasicrystals. An electrostatic repulsion force develops when the positively charged diffuse portions of double layers from two quasicrystals overlap in an aqueous suspension. Layer charge has little or no direct effect on double-layer swelling. The break up and formation of quasicrystals is a dynamic process that controls the average size of quasicrystals in an aqueous smectite suspension. As layer charge increases, quasicrystals tend to become larger and more stable. In smectite suspensions with more than one type of exchangeable cation, the cations can demix (e.g., Na and Ca may be segregated in different interlayer regions) due to a complex feed-back between cation exchange selectivity and crystalline swelling. Demixing influences the breakup and formation of quasicrystals because quasicrystals preferentially cleave along interlayers dominated by alkali cations. Increasing layer charge increases selectivity for alkaline earth cations relative to Na or Li, and hence reduces the breakup of quasicrystals. Co-volume swelling is an entropy driven process caused by restrictions on the rotational freedom of suspended quasicrystals. Brownian swelling is also an entropy driven process resulting from random thermal motion of suspended colloids. There is no reason to believe that layer charge directly influences either co-volume or Brownian swelling. Macroscopic measures of swelling (e.g., change in total volume or water content) necessarily measure the combined effect of all swelling processes occurring within the system.

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Keywords: Crystalline swelling; Layer charge; Smectite; Double-layer swelling; Co-volume swelling; Cation demixing

1. Introduction

The swelling of smectites is complex. Smectites swell by imbibing water or polar organic solvents between

smectite quasicrystals and/or between the individual layers within quasicrystals. Such swelling occurs when the clay is dispersed in a solvent, or when the clay is in direct contact with an atmosphere having a high vapor pressure of the solvent. Swelling also occurs when small interlayer cations are replaced by larger organic cations or by larger polymeric hydroxyl-metal cations. Each of the forms of swelling represents different processes and is controlled by different forces. Thus to fully understand the swelling of a specific smectite sample it is necessary

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to know the entire system, including: the amount of clay in the system relative to the liquid phase mass or volume, properties of the clay (purity, surface area, layer charge, morphology of the individual layers), nature and distributions of exchangeable and nonexchangeable interlayer cations, the quantity and activity of all solvents in the equilibrating solution or atmosphere, and the temperature of the system. Furthermore, some phases of smectite swelling are inherently hysteretic, hence one must also know the history of the sample. This review is focused on the influence of layer charge on the swelling of smectites in aqueous systems. Furthermore, the review is restricted to freely swelling smectites (interstratification of illitic or chloritic layers is not considered) saturated with alkali-metal or alkaline-earth cations only. Even with these restrictions, smectite swelling remains complex.

Before one can understand smectite swelling, one must first appreciate that smectites are organized in quasicrystals. Quasicrystals are sets of 2:1 phyllosilicate layers oriented with parallel *c* axes and randomly oriented *a* and *b* axes (Aylmore and Quirk, 1971). Each quasicrystal consists of between two to many thousands of individual layers stacked together. An example of smectite quasicrystals grouped together in a clay film imaged by transmission electron microscopy (TEM) is shown in Fig. 1. The dark, electron dense regions seen in the micrograph are the smectite quasicrystals. The light regions are holes or micropores between the quasicrystals. Three important observations derive from this micrograph: First, the individual quasicrystals are generally curved, suggesting that they are flexible. Second, individual quasicrystals are joined together forming the fabric of the film. And third, joins between quasicrystals are both face-to-face and edge-to-face. Fig. 2 is a high-resolution TEM micrograph showing a two-dimensional view of the arrangement of individual layers within a quasicrystal. The sub-parallel orientation of the individual layers is evident. Most of the layers are slightly to moderately curved, again suggesting that the individual layers are flexible. Some layers terminate within the middle of a quasicrystal, while others extend beyond the main body of the quasicrystal, suggesting that the individual layers have been randomly stacked. Some layers appear to have peeled off of the main body of the quasicrystal. These observations lead to a second critical point: quasicrystals are dynamic. Large quasicrystals may break up, forming several smaller quasicrystals and, conversely, several smaller quasicrystals may join together to form a single larger quasicrystal.

Six separate processes control swelling of smectites in aqueous systems: crystalline swelling, double-layer

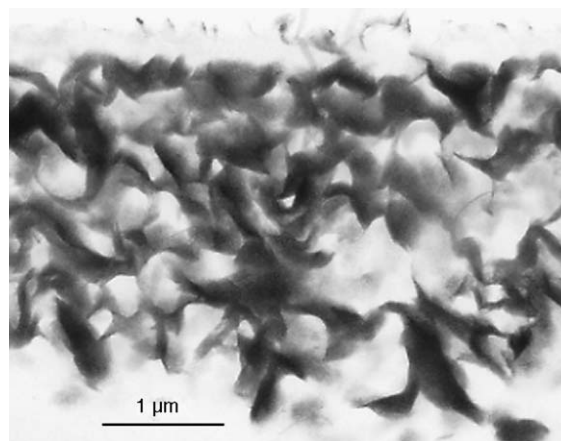


Fig. 1. Transmission electron micrograph of smectite quasicrystals grouped together in a clay film. The clay was saturated with tetradecylammonium cations, prepared as an oriented film, embedded in epoxy resin, and then sectioned with a diamond knife.

swelling, the breakup of quasicrystals, cation demixing, co-volume swelling, and Brownian swelling. The basic mechanisms and forces controlling each of these processes are different. One of these processes may dominate in a particular clay–water system, but generally three, four, five or even all six of these processes operate in concert to determine the swelling state of a sample. Following is a brief description of the mechanisms and forces controlling each of the swelling processes, along with an analysis of how layer charge influences each swelling process.

2. Crystalline swelling

Crystalline swelling is a process whereby 0 to 4 discrete layers of water molecules are intercalated between individual 2:1 layers (i.e., in the interlayer positions) within a smectite quasicrystal. Layer hydrates with 0, 1, 2, 3, and 4 layers of water molecules are distinguished by *d*001 (basal) spacings of approximately 10.0, 12.5, 15.0, 17.5 and 20.0 Å, respectively. Measured *d*-spacings often deviate from these ideal values, reflecting interstratification of several layer hydrates and/or differences in the packing arrangement of the interlayer water molecules. Free anions are excluded from the interlayers in the crystalline swelling range (Maréelja and Quirk, 1992), thus the interlayer cations stoichiometrically balance the negative surface charge arising from isomorphous substitution. Anions, however, may enter interlayers if they are part of a complex cation, such as an $(\text{OH})_y\text{Al}_x^{+(3x-y)}$ polymer.

Shown in Fig. 3a are X-ray diffraction patterns for a Mg-saturated sample of SPV bentonite (a Wyoming

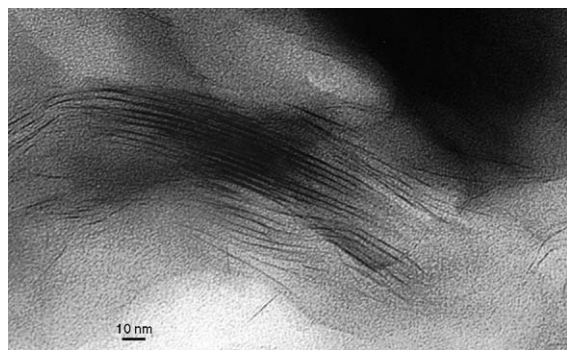


Fig. 2. High-resolution transmission electron micrograph showing the arrangement of individual layers within a smectite quasicrystal. The clay was saturated with octadecylammonium cations, prepared as an oriented film, embedded in epoxy resin, and then sectioned with a diamond knife (Laird et al., 1989).

bentonite) equilibrated with atmospheres controlled at 55, 75, 85, and 100% RH. At 55 and 75% RH the XRD patterns indicate average d -spacings of 15.29 Å, which is evidence that the samples are dominated by 2-layer hydrates. The average d -spacing (15.84 Å) for the sample equilibrated at 85% RH indicates that the sample is dominated by 2-layer hydrates but has a significant fraction of randomly interstratified 3-layer hydrates. The main XRD peak for the sample equilibrated at 100% RH is centered at $4.62^\circ 2\theta$ (19.13 Å), however the peak also has a broad shoulder stretching from about 5.0 to $5.8^\circ 2\theta$. The peak is interpreted as evidence for interstratification of layer hydrates with 2, 3, and 4 layers of interlayer water molecules. Shown in Fig. 3b is a histogram depicting proportions of the various layer hydrates in Mg-SPV bentonite as a function of RH. These data were obtained by modeling the XRD patterns shown in Fig. 3a using Newmod© (Reynolds and Reynolds, 1996).

Crystalline swelling is controlled by a balance between strong forces of attraction and repulsion (Norris, 1954; Kittrick, 1969) but is more easily modeled by considering potential energies of attraction and repulsion (Laird, 1996). The attraction potential energy is electrostatic and dominantly arises from the Coulombic attraction between the negative surface charge sites caused by isomorphous substitution and the positive charge of the interlayer cations. van der Waals interactions between adjacent layers may also contribute to the total potential energy of attraction. The potential energy of repulsion comes from the partial hydration potential energy of the interlayer cations and to a lesser extent the partial hydration potential energy of the negative surface charge sites. To understand the term “partial hydration potential energy”, consider a cation in the interlayer of a

smectite with two layers of interlayer water molecules. In such an environment, the cation is partially hydrated. Hence, the potential energy of repulsion contributed by the cation is related to the difference between the hydration state of the cation in the interlayer and the potential hydration state of the cation were in the equilibrating solution or atmosphere. When the relative humidity of an equilibrating atmosphere changes, or the activity of water in an equilibrating solution changes (for example, by adding salt to the solution), the potential hydration state of the cation changes even though the actual hydration state of the interlayer cation may not change. And, a change in the potential hydration state of an interlayer cation causes a change in the potential energy of repulsion.

An equation (Eq. (1)) relating the various potential energies (J m^{-2}) that are believed to control crystalline swelling was presented by Laird (1996). By convention, energies contributing to attraction between the layers are given negative signs, while those contributing to repulsion between the layers are given positive signs. On the

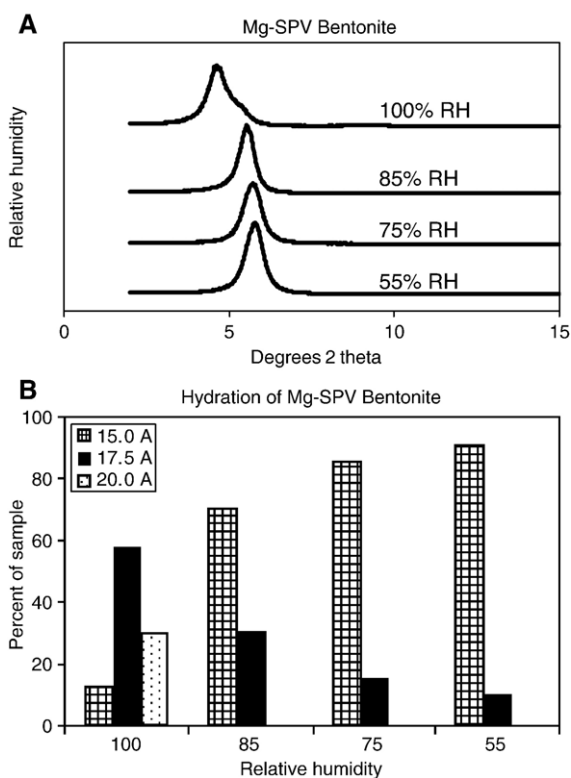


Fig. 3. A) X-ray diffraction patterns of Mg saturated SPV bentonite (a Wyoming bentonite) equilibrated with atmospheres controlled at 55, 75, 85, and 100% RH. B) histogram depicting proportions of the various layer hydrates in Mg-SPV bentonite as a function of RH. The XRD data were interpreted using Newmod© (Reynolds and Reynolds, 1996).

right side of Eq. (1) are terms for Coulombic attraction, van der Waals attraction, hydration repulsion, and Born repulsion, sequentially. The various symbols used in Eq. (1) are defined in Table 1.

$$\begin{aligned} \Delta G_{\text{rs}} = & - \left(\frac{z_i B \sigma^2 (D + r_s)}{\beta_1} \right) \\ & - \frac{H}{12B} \left(\frac{1}{(2D)^2} + \frac{1}{(2D + 2T)^2} - \frac{2}{(2D + T)^2} \right) \\ & + \left(\frac{\sigma z_i e}{2r_i} + \frac{\sigma e}{2r_s} \right) \left(\frac{1}{\beta_1} - \frac{1}{\beta_B} \right) + \frac{L}{(2D)^{12}} \end{aligned} \quad (1)$$

Crystalline swelling is inherently hysteretic (Laird et al., 1995). Crystalline swelling is a discrete process, because an interlayer can have 0, 1, 2, 3, or 4 layers of water molecules but cannot have 2.5 or any other fractional number of layers of water molecules (some variation of d -spacing about the ideal values is possible due to thermal expansion and contraction, but crystalline swelling is clearly a discrete process). By contrast, the relative humidity of an equilibrating atmosphere (or the activity of water in an equilibrating solution) can be varied continuously. Consider, for example, a Ca-smectite that is equilibrated against an atmosphere with a known relative humidity. For this system, the 15-Å phase (2 layers of interlayer water molecules) is stable over a large range of relative humidity (approximately 30 to 90% RH). As the relative humidity increases, from 30% to 90% the potential energy of attraction remains constant, because it depends on the d -spacing (in Eq. (1), d -spacing = $D + T$), which is constant. However, the potential energy of repulsion increases continuously with RH (in Eq. (1), β_B increases with RH). Eventually the potential energy of repulsion becomes so large that it

is able to overcome the mechanical resistance (ΔG_{rs}) and the Ca-smectite expands from a 2-layer hydrate to a 3-layer hydrate. The expansion decreases both the potential energy of attraction (because the interlayer cation and surface charge sites are separated by a greater distance (D increases)) and the potential energy of repulsion (because more water is intercalated and hence the partial hydration state of an interlayer cation is greater in a 3-layer hydrate than a 2-layer hydrate (β_1 increases)). If the relative humidity is then lowered, collapse will not occur at the same relative humidity as the previous expansion, because the potential energy of attraction is weaker for a 3-layer hydrate than a 2-layer hydrate. In Eq. (1), ΔG_{rs} increases or decreases to exactly balance the right side of the equation for a clay with a stable d -spacing.

From a thermodynamic perspective, it is important to recognize that a smectite in a chamber with a changing RH is not a closed system, because energy and matter must be put into or removed from the chamber to change the RH. When a smectite collapses, water molecules must be expelled from the interlayer, the layers must move closer together, and some rearrangement of the cations and remaining interlayer water molecules is inevitable. Conversely, when a smectite expands, new water molecules must be brought into the interlayer, the layers must move apart, and the interlayer water and cations again must be rearranged. These physical rearrangements of matter require work, and the energy needed to effect that work is lost from the chamber to the external universe during both expansion and collapse. In a strict sense, the different layer hydrates of a smectite are separate phases with different thermodynamic properties, and any transition from one layer hydrate to another is a phase change (Laird and Shang, 1997).

Slade et al. (1991) quantified decreased crystalline swelling of smectites with increasing layer charge by

Table 1
Definition of terms used in Eq. (1)

Term	Description	Value and units
ΔG_{rs}	Free energy due to mechanical resistance	Variable (J m^{-2})
E	Proton charge	$1.602 \times 10^{-19} \text{ C}$
β_B	Diabattivity of the bulk solution	$8.695 \times 10^{-9} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}$ (for DI water)
β_1	Diabattivity of the interlayer	Varies with D ; $\text{C}^2 \text{ N}^{-1} \text{ m}^{-2}$ (Laird, 1996)
H	Hamaker constant	$2.2 \times 10^{-20} \text{ J}$ (Quirk and Murray, 1991)
T	Thickness of a unit layer	$9.4 \times 10^{-10} \text{ m}$
D	Interlayer thickness	Between 6.0×10^{-11} and $1.3 \times 10^{-9} \text{ m}$
r_s	Effective radius of surface charge site	$4.7 \times 10^{-10} \text{ m}$
r_i	Effective radius of interlayer cation	Pauling radii plus $8.5 \times 10^{-11} \text{ m}$
σ	Surface charge density	Between 0.103 and 0.344 C m^{-2}
z_i	Interlayer cation valence	1, 2, or 3
L	Constant	$1.463 \times 10^{-124} \text{ J m}^{10}$

measuring d -spacings of smectites equilibrated with various NaCl solutions. Later Laird et al. (1995) verified the effect of layer charge on crystalline swelling and provided additional data quantifying hysteresis in crystalline swelling. In the Laird et al. (1995) study, five Na-smectites were initially equilibrated with 3.00 M NaCl. Then half of each sample was retained in 3.00 M NaCl while the other half was washed with

distilled water until Cl-free. The samples were then dialyzed against various final solutions ranging from 0.35 to 3.00 M NaCl for 14 days. During the dialysis the equilibrating solutions were refreshed a total of 5 times. A special liquid sample cell (Shang et al., 1995) allowed XRD analysis of the clays suspended in their final equilibration solutions. Fig. 4 shows the relationship between the measured d -spacings (d_{001} peak) and the

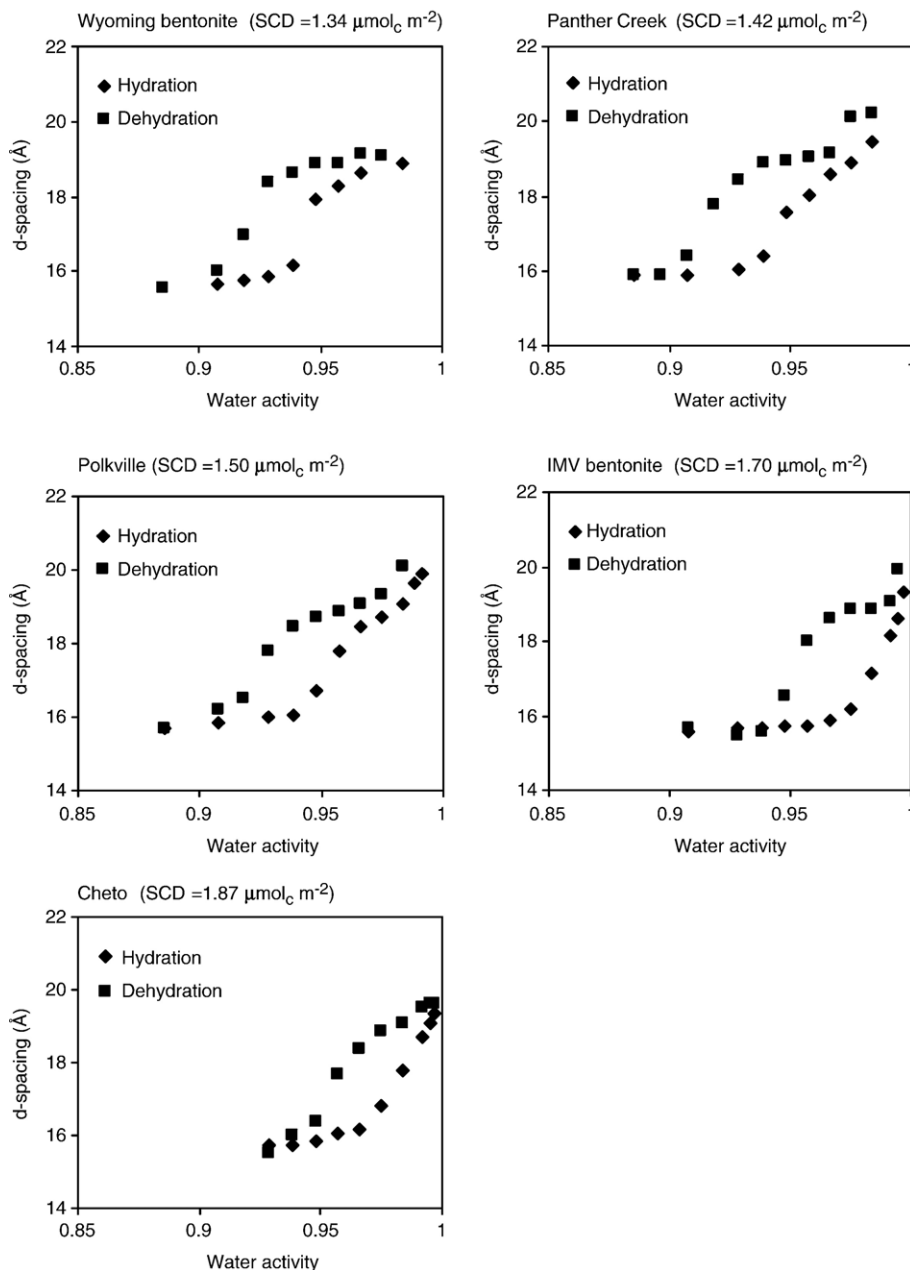


Fig. 4. The relationship between the measured d -spacings (001 peak) and the activity of water in equilibrating NaCl solutions for five reference smectites with different surface charge densities. Data are from Laird et al. (1995).

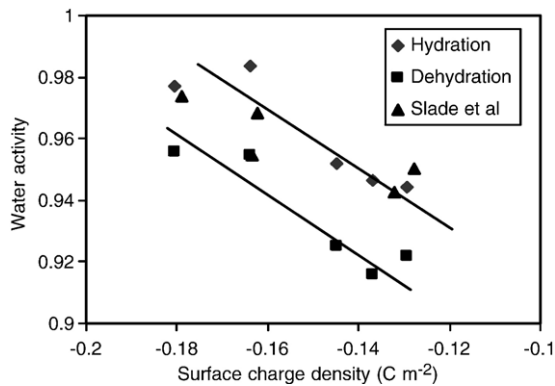


Fig. 5. The relationship between the average water activity for the 15.5 to 19.0 Å transition and surface charge density for both the hydration and dehydration transitions. The hydration and dehydration data are derived from the curves presented in Fig. 4 as originally presented by Laird et al. (1995). Results from a similar study (Slade et al., 1991) are presented for comparison.

activity of water in the equilibrating NaCl solutions for the five Na-smectites. The results clearly show hysteresis loops associated with crystalline swelling and a progressive increase in the activity of water at which both the hydration and dehydration transitions occur with increasing layer charge of the smectites. The average water activity for the 15.5 to 19.0 Å transition increased linearly with surface charge density for both the hydration and dehydration transitions (Fig. 5).

The fact that the activity of water needed to cause expansion or collapse increases with increasing layer charge (Fig. 5) is a clear indication that the potential energy of attraction increases more rapidly with increasing layer charge than does the potential energy of repulsion. This is so because the Coulombic attraction between the interlayer cations and the surface charge

sites increases with the square of the surface charge density (σ in Eq. (1)), whereas the potential energy of repulsion due to hydration potential of the interlayer cations and surface charge sites increases linearly with surface charge density. Hence, Eq. (1) predicts an increasing tendency of the clay to collapse with increasing layer charge (Table 2). Different results for the various cations shown in Table 2 are driven by differences in the effective radius (r_i) of the different cations. The data presented in Table 2 were obtained by assuming that ΔG_{TS} is equal to zero. This assumption is equivalent to assuming that crystalline swelling is both continuous and reversible. Although the assumption is clearly wrong, the resulting error is small, as the results presented in Table 2 are generally consistent with experimental evidence (MacEwan and Wilson, 1980).

3. Double-layer swelling

Crystalline swelling is a process that occurs within quasicrystals; in contrast double-layer swelling is a process that occurs between quasicrystals. Most of the total surface charge on smectites is expressed within the interlayers of quasicrystals and does not participate in formation of diffuse double layers (DDL). However, a small portion of the total charge is expressed on the external surfaces of a quasicrystal. The negative charge on an external surface forms one half of the electric double layer. And a net positive charge in the solution adjacent to the external surface forms the other half of the electric double layer. The positive charge develops because exchangeable cations are weakly held by the external surfaces and tend to diffuse from regions of high concentration adjacent to the surface towards regions of low concentration in the bulk solution. The diffusion of the cations is opposed by the electrostatic

Table 2
Effect of layer charge and exchangeable cation on basal spacings of expanding 2:1 phyllosilicates as predicted by Eq. (1)

Interlayer cation	Layer charge [per $\text{O}_{10}(\text{OH})_2$]				
	0.3	0.4	0.5	0.6	0.7
	– d -spacing (Å)–				
Li	22.8	20.6	18.6	16.8	15.1
Na	21.5	19.1	17.0	15.0	13.2
K	20.4	17.8	15.5	13.3	9.95
Rb	20.0	17.3	14.9	12.5	9.95
Cs	19.5	16.7	14.2	9.95	9.95
Mg	21.7	19.3	17.1	15.2	13.5
Ca	20.3	17.6	15.2	13.2	9.96
Sr	19.5	16.6	14.2	11.9	9.95
Ba	19.5	16.7	14.2	9.95	9.95

The numerical solution to Eq. (1) was obtained by assuming that ΔG_{TS} is zero and that the samples are equilibrated with DI water (from Laird, 1996).

attraction between the positive charge of the cations and the negative surface charge. At the same time, anions from the bulk solution diffuse toward the region of low anion concentration near the surface but are retarded by the electrostatic repulsion from the negatively charged surfaces.

The separation of negative surface charge from the positive charge of the compensating cations in the diffuse portion of the double layer is responsible for the colloidal behavior of smectites in suspensions. When by Brownian motion two colloids approach each other in solution such that the positively charged, diffuse regions of their respective double layers begin to overlap, an electrostatic repulsive force develops. This repulsive force stabilizes colloidal suspensions. Following is a brief discussion of the basic equations that describe DDL phenomena. The reader is referred to Verwey and Overbeek (1948), Singh and Uehara (1986), Van Olphen (1987), and Güven (1992) for more complete discussions and derivations of DDL equations.

The fundamental Gouy–Chapman equation for permanent charge surfaces describes the relationship between surface charge density (σ), surface potential (ψ_o), valence of the compensating cations (z_+), and the electrolyte concentration of the bulk solution (c_o),

$$\sigma = (2c_o \varepsilon_r \varepsilon_o RT / \pi)^{1/2} \sinh(z_+ F \psi_o / 2RT) \quad (2)$$

where ε_r is the relative permittivity of the medium, ε_o is the permittivity of a vacuum, F is the Faraday constant, R is the gas constant, and T is temperature in Kelvin. Eq. (2) can be rearranged to express the surface potential as a function of the surface charge density:

$$\psi_o = (2RT / z_+ F) \sinh^{-1}(\sigma / (2c_o \varepsilon_r \varepsilon_o RT / \pi)^{1/2}) \quad (3)$$

The Poisson–Boltzmann equation describes the influence of surface potential, the bulk solution electrolyte concentration (c_o), and valence (z) on the electrical potential of the diffuse region (ψ) between the surface and some distance (x) from the surface.

$$\frac{d^2 \psi}{dx^2} = \frac{8\pi z F c_o}{\varepsilon_r \varepsilon_o} \sinh \frac{z F \psi_o}{RT} \quad (4)$$

After two integrations, the Poisson–Boltzmann equation can be rewritten to predict the local electrical potential (ψ_x) at some distance (x) from the surface:

$$\psi_x = \frac{2RT}{zF} \ln \left(\frac{\exp(\kappa x) + \tanh(\lambda)}{\exp(\kappa x) - \tanh(\lambda)} \right) \quad (5)$$

where:

$$\kappa = \left(\frac{8\pi z^2 F^2 c_o}{\varepsilon_r \varepsilon_o RT} \right)^{0.5} \quad \text{and} \quad \lambda = \left(\frac{z F \psi_o}{4RT} \right).$$

The Boltzmann equation relates the local cation (c_+) and anion (c_-), concentrations to the local electrical potential and the bulk solution ionic concentration,

$$c_+ = c_o \exp(-z_+ e \psi_x / kT) \quad (6)$$

$$c_- = c_o \exp(z_- e \psi_x / kT) \quad (7)$$

where e is the proton charge and k is the Boltzmann constant.

Stern (1924) recognized that under some conditions DDL theory predicts impossibly high surface potentials. He suggested that some cations would be tightly held adjacent to the surface and that anions would be excluded from this zone. The so-called *Stern layer* has the effect of reducing the surface potentials that control the diffuse double layers by an amount proportional to the fraction of the surface charge density that is neutralized by cations in the Stern layer. The Stern layer is thought to be approximately the thickness of the hydrated diameter of the adsorbed cations (i.e., a monolayer of adsorbed hydrated cations). Thermal motion will constantly introduce new cations to the Stern layer and eject others back into the diffuse region of the double layer, however, the proportion of the surface charge neutralized by cations in the Stern layer will remain constant unless the system is perturbed. Increasing the valence of the exchangeable cations, increasing the salt concentration in the bulk solution, and/or decreasing the hydration energy of the exchangeable cations all tend to increase the fraction of the surface charge neutralized by the cations in the Stern layer (Shainberg and Kemper, 1966).

Eq. (3) predicts that surface charge density will have a small effect on surface potentials (Fig. 6) over the range of surface charge (-0.02 to -0.20 C m^{-2}) associated with smectites. The range in surface charge density covered in the analysis stretches from a high charge smectite with no Stern layer (-0.20 C m^{-2}) to a low charge smectite with $>80\%$ of the surface charge satisfied by Stern layer cations (-0.02 C m^{-2}). By combining Eqs. (3), (5), (6), and (7), we find that the small differences in surface potential have almost no effect on the relationship between local electrical potential and distance (Fig. 7a and b) and on the relationship between the local concentrations of cations and

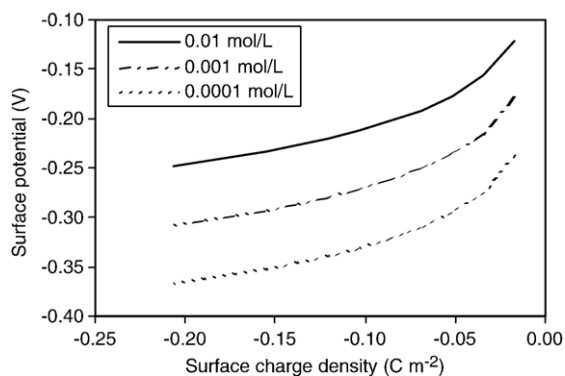


Fig. 6. The effect of surface charge density on surface potentials as predicted by the Gouy–Chapman equation (see text Eq. (3)) over the range of surface charge density values possible for smectites (-0.02 to -0.20 C m^{-2}).

anions and distance (Fig. 7c). This analysis predicts that the surface charge density of smectites has almost no effect on the electrostatic repulsive force between quasicrystals and hence on the stability of smectite suspensions. In contrast, both ionic strength and valence have much greater influences on the relationship between the local electrical potential and distance and ionic concentration versus distance relationship (Figs. 8 and 9). Thus DDL theory is consistent with the common observation that the stability of smectite colloidal systems increases with decreasing electrolyte concentration and decreasing valence of the compensating cation, but fails to predict the observation that low-charge smectite suspensions are generally more stable than high-charge smectite suspensions.

Many discussions of colloidal stability balance the double layer electrostatic repulsion with a long-range attractive force attributed to van der Waals interactions (DLVO theory). After many decades of research the validity of the diffuse double layer theory (Low, 1980) and especially the role of van der Waals forces in colloidal systems remains controversial. Recently, several authors have suggested that osmotic swelling pressure is opposed by a long range Coulombic attraction force between the surfaces and the counterions (Sogami and Ise, 1984; Smalley, 1994; McBride, 1997; McBride and Baveye, 2002). In the opinion of the author, there is a substantial body of evidence to support long-range double layer repulsion but the role of long-range van der Waals attractive forces is dubious for smectite suspensions due to the challenge of propagating van der Waals interactions through an aqueous medium. The proposed long-range Coulombic attraction theory is also questionable because it does not appear to account for field electrostatic repulsion within the overlapping diffuse

regions of opposing double layers. On the other hand, this leaves unanswered the nature of long-range attractive force, and McBride and Baveye (2002) have made a strong argument for the existence of such a force. At present, the controversy continues (Quirk, 2003; McBride and Baveye, 2003).

Experimental evidence of the relationship between double-layer swelling and layer charge is equivocal. Foster (1953) found no relationship between layer charge and a macroscopic measure of swelling volume for 12 Na-smectites. By contrast, Low (1980) found generally increasing water content with increasing cation exchange capacity for Na-smectites equilibrated at suction pressures between 0.025 and 3 atm. However, crystalline swelling, double-layer swelling, and the breakup and formation of quasicrystals are confounded in both of these studies, hence neither provides a clear analysis for the relationship between double-layer swelling and layer charge. Perhaps the best experimental evidence comes from low-angle XRD measurements of interparticle spacings. In a classic paper, Norrish (1954) demonstrated an inverse relationship between interparticle separation and the inverse square root of the solution electrolyte concentration. Norrish did not study the effect of layer charge on interparticle separations. However, Viani et al. (1983) measured interparticle separations for eight Na-smectites equilibrated at various pressure potentials and observed little or no effect of surface charge density on double-layer swelling.

4. Formation and breakup of quasicrystals

The dynamic nature of quasicrystals is a unique feature of smectite suspensions. When two smectite quasicrystals approach each other in an aqueous suspension with sufficient kinetic energy to overcome the double layer repulsion the diffuse portions of their double layers will begin to fuse. As this occurs anions, excess cations, and water are expelled from the region between the two approaching surfaces. If the two surfaces approach close enough ($<4 \text{ nm}$) and enough anions and excess cations are expelled, the electrostatic forces will undergo a complete reversal from being repulsive in the double layer region to attractive in the crystalline swelling region. The result is that two quasicrystals join together forming one larger quasicrystal. Conversely, hydrodynamic forces caused by shaking, stirring, raindrop impact, etc. may shear a large quasicrystal forming two separate but smaller quasicrystals. Na- and Li-saturated smectites in dilute aqueous systems can be almost completely delaminated such that diffuse double layers form between all of the individual layers and each layer

behaves as a separate colloid. The breakup and formation of quasicrystals is graphically illustrated in Fig. 10.

The existences and hence apparent stability of quasicrystals in aqueous suspensions, even of Na- and Li-smectite suspensions, has been clearly demonstrated by viscosity, light scattering, and neutron scattering studies (Sposito, 1992). However, despite the obvious importance to smectite swelling, the breakup and formation of quasicrystals has not been extensively studied. An ex-

ception is the work of Greene et al. (1973), who noted that CaCl_2 concentration was inversely related to the time required to form quasicrystals; an observation that is consistent with double layer repulsion forming an energy barrier between approaching colloids. In aqueous suspensions, the interlayer spacing within quasicrystals is fixed (controlled by crystalline swelling), thus when a smectite sample is dispersed by agitation (stirring, shaking, sonicating, etc.), the primary physical

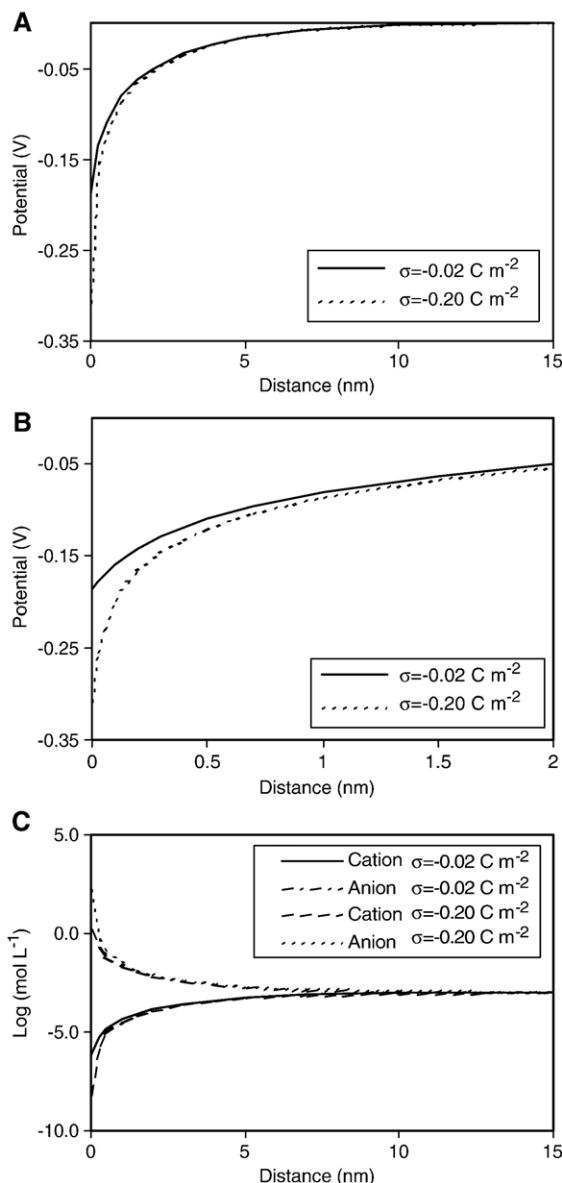


Fig. 7. A) the effect of small differences in surface potential on the relationship between local electrical potential and distance within the diffuse region of the electric double layer. B) the same relationship as shown in (A) but with a different scale to show differences due to surface charge. C) the relationship between the local concentrations of cations and anions and distance within the diffuse region of the electric double layer. Data are presented for surface charge values of -0.02 and -0.20 C m^{-2} , which covers the range of possible surface charge for smectites.

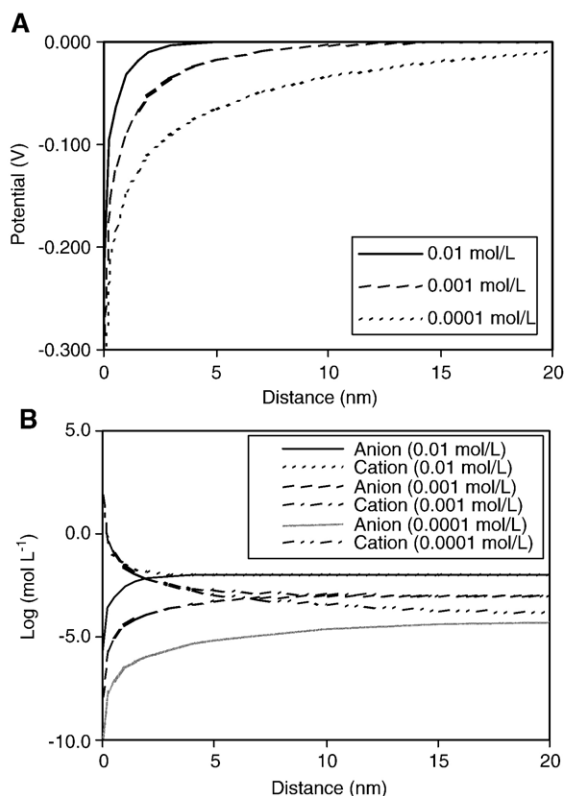


Fig. 8. A) the effect of ionic strength on the relationship between the local electrical potential and distance within the diffuse region of the electric double layer. B) the effect of ionic strength on local cation and anion concentrations within the diffuse region of the electric double layer.

change is the breakup of big quasicrystals into many little quasicrystals. A simple calculation illustrates the importance of the process. 1 g of dehydrated clay with a particle density of 2.65 g cm^{-3} occupies 0.377 cm^3 . The same gram of clay with four layers of interlayer water molecules occupies 0.755 cm^3 . And if the clay is delaminated, such that the spacing between each layer is 10 nm, the 1 g of clay will occupy 3.77 cm^3 .

The effect of layer charge on the breakup and formation of smectite quasicrystals has not been studied. However, the extent of crystalline swelling (d -spacing) is known to decrease with increasing layer charge (see discussion above under Crystalline swelling) and this decrease should increase both the size and stability of quasicrystals. Therefore it is reasonable to assume that as layer charge increases the quasicrystals will become larger and more stable. If this assumption is correct, then quasicrystal dynamics explains the observation that low-charge smectite suspensions are generally more stable than high-charge smectite suspensions, an observation that cannot be explained by diffuse double layer theory.

5. Cation demixing

The nature of the exchangeable cations adsorbed on smectite surfaces has a dominating influence on smectite swelling behavior. Smectites saturated with strongly hydrated monovalent cations (e.g., Na and Li) readily swell. When placed in distilled water or a dilute electrolyte solution, most quasicrystals of low-charge Na-smectites will spontaneously breakup such that diffuse double layers form and separate the individual smectite layers. For high-charge, Na-smectite, some quasicrystals will remain intact, but most will at least partially breakup. The addition of kinetic energy by stirring, shaking or sonicating is usually all that is required to disperse a Na- or Li-smectite in distilled water. By contrast, when a Mg- or Ca-saturated smectite is placed in distilled water the d -spacings typically expand from 15 Å (air dry Ca- or Mg-smectite) to 19 Å (Ca- or Mg-smectite in distilled water), but the quasicrystals do not spontaneously delaminate. Stirring, shaking or even sonication will cause some big quasicrystals to break up,

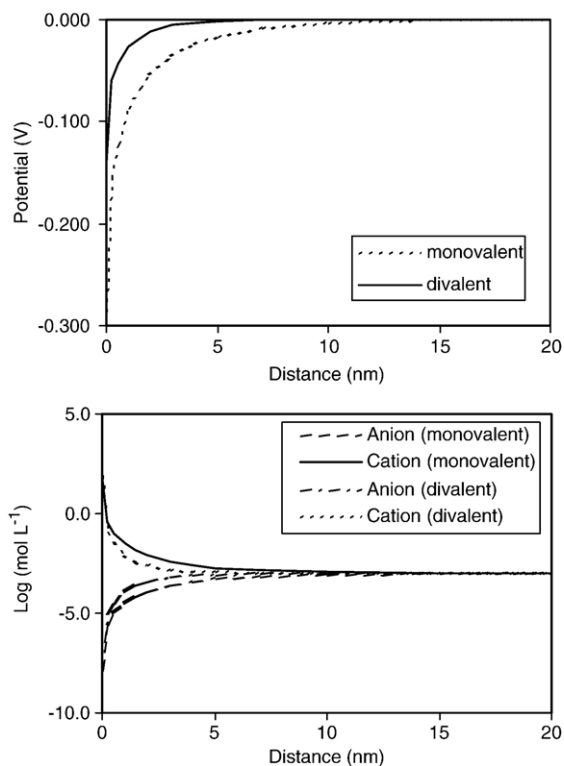


Fig. 9. A) the effect of valence on the relationship between the local electrical potential and distance within the diffuse region of the electric double layer. B) the effect of valence on the relationship between the local cation and anion concentrations within the diffuse region of the electric double layer.

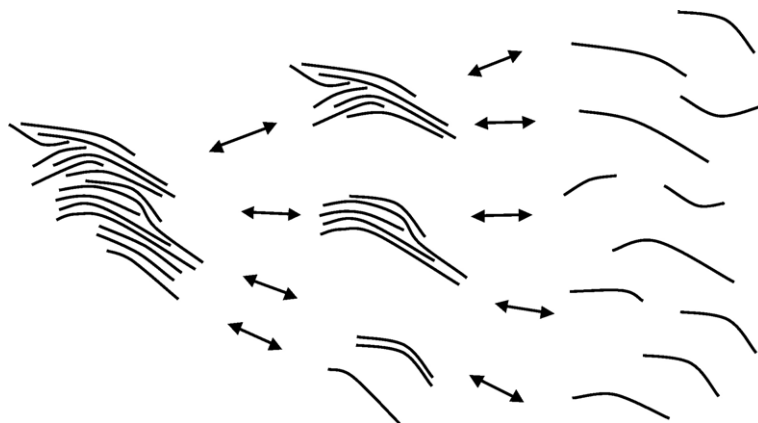


Fig. 10. Schematic diagram depicting the breakup and formation of quasicrystals. On the left the layers are grouped together in a single quasicrystal. In the middle the same layers are split into four quasicrystals. And, on the right the layers are completely delaminated.

forming a suspension of smaller Ca- or Mg-smectite quasicrystals. But most (if not all) Ca-smectites cannot be delaminated even by vigorous sonication.

When two different types of cations (e.g., Na and Ca) are present in an aqueous smectite system, the smectite may exhibit distinct preference for one cation over the other. Such cation exchange selectivity is governed by a complex feed-back process, whereby the extent of crystalline swelling controls selectivity for one cation relative to another, selectivity as well as the composition of the equilibrating solution controls the mix of cations in the interlayers, and the mix of cations in the interlayers and other clay and solution properties control the extent of crystalline swelling (Laird and Shang, 1997). The demixing of cations is one consequence of this complex feed-back system. In a Na/Ca-smectite system for example, demixing means that Na ions will tend to be segregated in certain interlayers while the competing

Ca ions are segregated into other interlayers. When the clay is shaken, the quasicrystals will readily break apart at interlayers dominated by Na (Fig. 11). The phenomenon of demixing is a major reason why a relatively small amount of Na can be so disruptive to soil structure (Shainberg and Otoh, 1968).

Layer charge influences demixing primarily through the interaction between swelling and cation exchange selectivity. As a general rule, selectivity for a divalent cation relative to Li or Na increases as layer charge increases (Maes and Cremers, 1977; Laird and Shang, 1997). By contrast, selectivity for weakly hydrated monovalent cations (K, Rb, or Cs) relative to Ca or Mg actually increases with increasing layer charge. This reversal in selectivity is due to an increasing tendency of interlayers for highly charged smectites to collapse when saturated with weakly hydrated monovalent cations. Both conditions, however, lead to increasing size

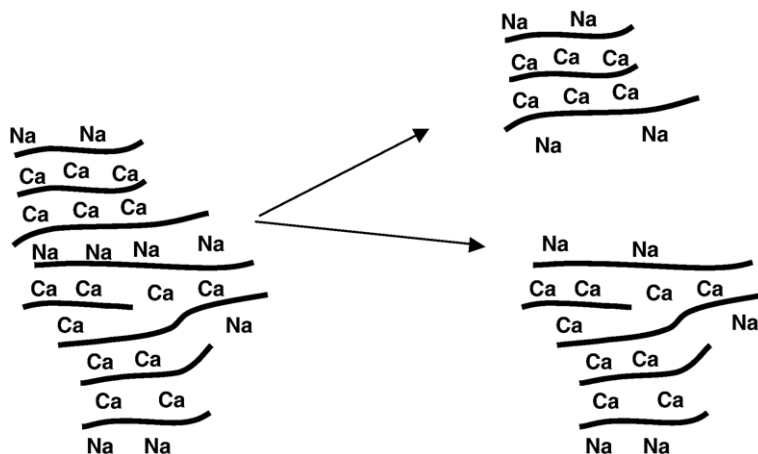


Fig. 11. Schematic diagram depicting demixing of Ca and Na and the preferential breakup of smectite quasicrystals along interlayers dominated by Na.

and stability of the quasicrystals with increasing layer charge. Thus increasing layer charge tends to inhibit the breakup of quasicrystals and hence to decrease swelling in mixed cation systems.

6. Co-volume swelling

Water molecules are constantly colliding with colloidal particles in aqueous suspensions. Each collision transfers kinetic energy either from the water molecule to the colloid or vice versa. The result is that suspended colloids are in constant motion (referred to as thermal or Brownian motion). If the collisions are unbalanced, a colloid will have net movement in one direction, i.e. diffusion. However, colloids are also in constant rotational motion. Because individual smectite layers are anisometric, their longest dimension determines their minimum free rotational volume. Furthermore, when two freely rotating smectite layers approach each other, their first interaction will be due to the intersection of the diffuse portions of their double layers, which will result in a repulsive force before the layers actually touch. Hence, the effective rotational volume is determined by the longest dimension of the layer plus twice the length of the double layer (Fig. 12). A few simple calculations using the equation for the volume of a sphere ($V_s = 4/3\pi r^3$) illustrates the importance of co-volume swelling. First, if we assume the longest dimension of a mono-dispersed disk shaped smectite layer is 300 nm and that the double layer thickness is 5 nm; then the effective radius of the particle is 160 nm and the minimum rotational volume is $1.7 \times 10^7 \text{ nm}^3$ or 243 times the volume of the smectite layer. Second, assuming 1 g of smectite is completely delaminated, the particle density is 2.65 g cm^{-3} , all of the particles are perfect 1 nm thick disks exactly 300 nm in diameter, and the rotational volumes of each layer are in a perfect hexagonal close packing arrangement; then the minimum co-volume for that 1 g of clay is 124 mL. The actual co-volume of a real delaminated smectite sample will be much larger because smectite layers are not uniform perfect disks. A co-volume of 300 mL is probably more realistic for 1 g of fully dispersed smectite. Such large co-volumes mean that, in all but the most dilute suspensions, the rotational freedom of dispersed smectite layers is severely limited, and that individual layers tend to align with their neighbors. If more water is carefully (without mixing) and isothermally added to the top of such a suspension, the colloidal suspension will expand into the new water volume. The driving force for this expansion is an increase in entropy due to the increased rotational freedom of the smectite colloids.

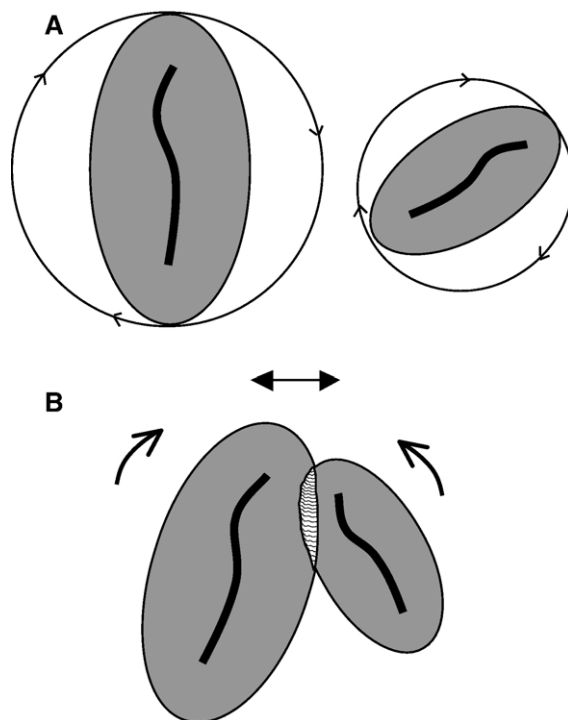


Fig. 12. Schematic diagrams depicting co-volume: A) co-volume is the volume about a particle and the associated diffuse double layer that allows complete rotational freedom. B) when diffuse double layers of two rotating particles intersect a repulsive force develops inhibiting free rotation.

There is no reason to believe that layer charge will have a direct effect on co-volume swelling of a mono-dispersed smectite suspension. However, most smectite suspensions are a mixture of individual layers and small quasicrystals. As discussed previously, quasicrystals are dynamic; new ones are constantly forming while others are breaking apart. Theoretically, layer charge will influence the amount of kinetic energy required to both form and breakup a quasicrystal, and hence the size and average number of layers per quasicrystal in a suspension. Thus, macroscopic measures of total swelling in the “co-volume swelling range” are anticipated to show an inverse relation with layer charge. The effect, however, would be due to quasicrystal dynamics not co-volume swelling *per se*. I am not aware of any experimental work in which quasicrystal dynamics and co-volume swelling have been independently quantified.

7. Brownian swelling

Brownian swelling is the ultimate state of dispersion/delamination for a smectite. In the Brownian swelling range the individual layers are so widely dispersed in an aqueous suspension that there is no interaction between

the neighboring layers. Due to random thermal motion, individual layers are more likely to diffuse away from a zone of relatively high concentration and towards a zone of relatively low concentration of other layers. Brownian swelling of smectites is an entropy-driven process. There is no reason to believe that layer charge will have any influence on Brownian swelling of smectites.

8. Summary and conclusions

The swelling of smectites is complex. This review has focused on the six processes that control the swelling of smectites in aqueous systems and specifically on how those processes are influenced by the layer charge of smectites. In any given aqueous system, several of these processes may occur simultaneously and their combined impact determines macroscopic measures of swelling. Key to understanding smectite swelling is appreciating the dynamic nature of smectite quasicrystals and differences between the swelling that occurs within quasicrystals (crystalline swelling) and the swelling that occurs between quasicrystals (double-layer, co-volume, and Brownian swellings). As a general rule, an increase in layer charge results in decreased crystalline swelling (smaller d -spacings) and increases in both the size and stability of smectite quasicrystals. Layer charge has little or no direct effect on double-layer swelling, co-volume swelling, or Brownian swelling. However, because layer charge influences the size and stability of quasicrystals, layer charge may have an indirect effect on double-layer and co-volume swellings. In mixed cation–smectite systems, layer charge has a large influence on cation exchange selectivity and hence on the relative proportions and distributions of the various cations on the interlayer and external surface exchange sites. Demixing of cations, where, for example, Na preferentially concentrates in certain interlayers, has a large influence on the breakup and formation of quasicrystals and thereby on swelling.

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